

## PILOT-PLANT STUDY OF FLOCCULATION OF SUSPENDED SOLIDS IN LIME-SULFIDE UNHAIRING EFFLUENTS\*

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### Abstract

We have studied the removal of suspended solids from commercial unhairing effluents by means of a pilot-plant continuous flow apparatus. Effluents were obtained from tanneries which processed either fresh or salt-cured hides in paddle vats or hide processors. Approximately 80 to 85 percent of the suspended solids were removed from the effluents tested. The results substantiate earlier laboratory studies that established the ranges of effluent compositions (pH, salt content, suspended solids, and soluble organic content) for which specific flocculation treatments are effective.

### Introduction

In previous studies at the Eastern Regional Research Center we investigated the ranges of composition variables (pH, salt content, suspended solids, and soluble organic content) in which specific flocculation treatments are effective in removing the suspended solids from commercial unhairing solutions (1-3). The composition of different lime-sulfide unhairing effluents influences the efficiency of specific flocculation treatments for them. Thus, the effluent from a hide processor unhairing operation, which contains high levels of suspended solids and other constituents, and effluent from a paddle-vat unhairing operation require different flocculation treatments.

Certain synthetic organic polymers of high molecular weight are capable of greatly increasing the flocculation rate when added in ppm amounts. Nonionic, anionic, or cationic polymers are strongly adsorbed on the minute suspended solid particles. The long chain length and many active sites on the polymers allow them to be adsorbed on the fine particles by a bridging action, forming large and dense floc particles with high settling rates (4).

The main problems of pollution resulting from the tannery beamhouse are the

volumes of unhairing waste and its concentrations of BOD, COD, suspended matter, and salinity. Recycling of unhairing waste conserves water and can at the same time decrease pollution of the environment if the residues are properly handled. Dhar (5) claims that the use of enzymes in soaking, unhairing, and bating can decrease the volumes of tannery unhairing waste and eliminate the need for large volumes of water. The main purpose of a primary treatment system is to reduce the solids loading. Substantial reductions in costs can result from efficient operation of flocculation and sedimentation.

Our earlier studies were conducted with laboratory bench-scale equipment. This paper reports the removal of suspended solids by flocculation treatments from several different types of unhairing effluents by means of a pilot-plant continuous flow apparatus.

## Experimental

The unhairing wastes used in these studies were obtained from four tanners who unhair cattlehides by different procedures. One tanner processes fresh cattlehides in a paddle vat, the second processes brine-cured hides in a paddle vat, the third processes brine-cured hides in a drum and recycles the unhairing solution, while the fourth processes salt-cured hides in a hide processor.

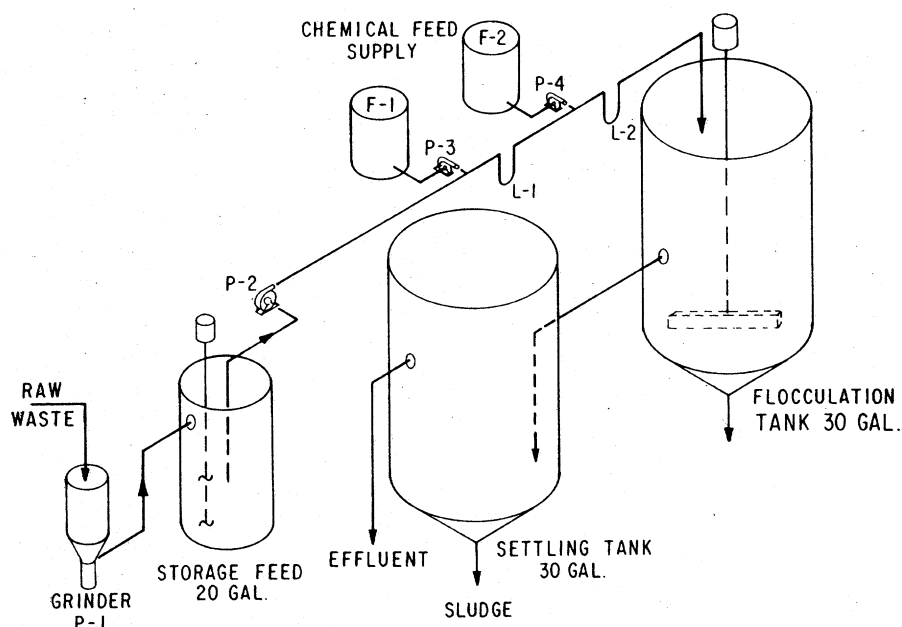


FIGURE 1. — Pilot plant for flocculation experiments.

Fat was skimmed off each waste when it was received, and each waste was then passed through a Moyno† progressing cavity pump which is capable of grinding particles up to 1-1/8 in. in diameter to uniformly fine particles. The waste was pumped into a storage feed tank prior to treatment. The continuous flow treatment of each unhairing waste is shown schematically in Figure 1.

Each waste was stirred continuously and pumped from the storage feed tank by means of a Masterflex pump into a 1-in. diameter plastic pipe. Flocculant was added to the stream at individual ports in the plastic pipe at a rate of 10 ml/min/l of waste. The waste was pumped at a rate of 6 gal/hr through the system. The waste, together with flocculant, was passed through two loops of 10 ft each of 1-in. diameter polyethylene tubing to thoroughly mix the flocculant with the waste. The estimated detention time in the loops was 4 min. The flow continued into a 30-gal flocculation tank, with a working volume of 12 gal, and was slowly stirred at about 25 rpm to promote floc formation. The resulting mix flowed into a settling tank with a 2-hr retention time. Samples were taken from the effluent overflow at hourly intervals for analyses of suspended solids.

#### UNHAIRING WASTES

Since different types of wastes can result from unhairing different kinds of cattlehides—*e. g.*, fresh hides, brined hides, dry-salted hides—these wastes can contain different amounts of salt. To study the effects of salt on the flocculating ability of chemical flocculants, we added 2 and 5 percent NaCl (based on the volume of waste) to fresh hide paddle-vat unhairing waste. We also studied the effects of chemical flocculation on several additional types of wastes from the unhairing of brine-cured hides in a paddle vat, of brined-cured hides in a drum, and of salt-cured hides in a hide processor.

#### FLOCCULATING AGENTS

The polyelectrolytes used to induce flocculation of suspended solids in the unhairing wastes were those found to be optimum in our earlier laboratory studies (1-3). Rohm and Haas Company products PFA-10 (anionic), PFC-3 (cationic), and sodium hexametaphosphate were used to flocculate the paddle vat, recycle, and drum unhairing wastes. Estech, Inc., product X-400 (anionic) was used to flocculate the hide processor waste.

#### COMPOSITION VARIABLES

The effects of flocculation on the fractions separated in the pilot plant were studied. These fractions were: original waste, flocculated solids, and supernatant liquor. The following composition variables in each fraction were deter-

†Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

mined: total solids, suspended solids, volatile solids, chemical oxygen demand (COD), sodium sulfide, total nitrogen, total fat, total ash, and calcium oxide.

#### ANALYTICAL METHODS

The official methods of analysis of the American Public Health Association, American Water Works Association, and Water Pollution Control Federation were used for the determinations of COD, total solids, suspended solids, and volatile solids (6). Total nitrogen was determined by the Kjeldahl method, with a Technicon Industrial Systems Method 376-75-WA (7). Sodium sulfide was determined by the Official Method of Analysis of the Society of Leather Trades' Chemists (8). Calcium oxide was determined (after dissolving the total ash in hydrochloric acid, filtering, and diluting to the proper volumes) with a Perkin-Elmer Model 306 atomic absorption spectrophotometer equipped with a triple-slot burner (9, 10).

### Results and Discussion

The first step in reducing the solids loading of tannery unhairing waste is primary treatment. Substantial reductions can be achieved by the use of chemical flocculants. The results obtained in these studies substantiate earlier laboratory studies that established the ranges of unhairing effluent compositions for which specific flocculant treatments are effective. For example, Cooper *et al.* (1) reported that a flocculant system comprising PFA-10, PFC-3, and  $(\text{NaPO}_3)_6$ , in a certain combination, would reduce the suspended solids of paddle-vat unhairing waste by 90 to 98 percent in laboratory studies. Bitcover *et al.* (2) reported that X-400 would likewise reduce the suspended solids of hide processor waste by 90 to 95 percent. We used the recommended concentrations of these flocculants in the flocculation pilot plant. Table I summarizes the per-

TABLE I  
EFFECT OF FLOCCULANTS ON REMOVAL OF SUSPENDED SOLIDS  
FROM FRESH HIDE PADDLE-VAT UNHAIRING WASTE

| Flocculant                          | Concentration   | Percent removal |
|-------------------------------------|-----------------|-----------------|
|                                     | (mg/l)          | (%)             |
| Control (no flocculants)            |                 | 29.4            |
| PFA-10                              | 3               | 86.5            |
| PFC-3                               | 3               | 48.0            |
| $(\text{NaPO}_3)_6$                 | 30              | 64.0            |
| Combination (all three flocculants) | 36 <sup>a</sup> | 76.3            |

<sup>a</sup> PFA-10, 3 mg/l; PFC-3, 3 mg/l;  $(\text{NaPO}_3)_6$ , 30 mg/l

cent removal of suspended solids from fresh hide paddle-vat unhairing waste in such a series of trials.

The control indicates that about 30 percent of the suspended solids are removed by gravity settling for 2 hr. The use of each flocculant at the designated concentrations removed the indicated percentages of suspended solids. The combination of all three flocculants, however, removed about 10 percent less of suspended solids than PFA-10 alone; therefore, we decided to use only PFA-10 in further experiments with this waste.

Earlier laboratory tests (3) indicated that the NaCl content of an unhairing waste under usual conditions is not a primary factor in the flocculating efficiency of polyelectrolytes. However, there are certain times when substantial amounts of salt may be present due to types of hides and unhairing procedures. In these studies it was necessary to store some unhairing wastes for several days or a week before being processed. Consequently, it was deemed advisable to study the effects of added salt and holding period (age) on the flocculation of suspended solids. The results of this study are summarized in Table II.

The control, with no added salt and no added flocculant, showed an initial reduction of suspended solids of 27 percent due to gravity settling. The addition of chemical flocculant (PFA-10) showed an initial reduction of suspended solids of 91 percent. The addition of up to 5 percent NaCl did not appreciably affect the reduction in suspended solids. There was a 10 percent reduction in flocculant efficiency at the 8 percent salt level. Since paddle-vat unhairing waste from fresh hides usually contains less than 0.2 percent NaCl, salt content is unlikely to be an important factor under typical unhairing conditions. Table II shows that holding periods up to 3 weeks (with no added NaCl) resulted in only a small decrease in flocculant efficiency (91 to 85 percent removal of suspended solids). The combined effects of increased salt content and prolonged holding

TABLE II  
EFFECTS OF ADDED SALT AND AGING ON FLOCCULATION OF  
FRESH HIDE PADDLE-VAT UNHAIRING WASTE <sup>a</sup>

| Aged<br>(weeks) | Removal of suspended solids |         |         |         |         |
|-----------------|-----------------------------|---------|---------|---------|---------|
|                 | Control <sup>b</sup>        | 0% NaCl | 2% NaCl | 5% NaCl | 8% NaCl |
|                 | (%)                         | (%)     | (%)     | (%)     | (%)     |
| 0               | 26.8                        | 91.2    | 83.8    | 89.8    | 80.2    |
| 1               | 28.3                        | 91.8    | 83.1    | 78.0    | 67.6    |
| 2               | 28.5                        | 81.8    | 78.0    | 78.0    | 60.0    |
| 3               | 20.7                        | 84.8    | 70.3    | 66.6    |         |

<sup>a</sup> Flocculant: PFA-10, 3 mg/l of effluent.

<sup>b</sup> No flocculant added.

TABLE IV

EFFECT OF ADDED SALT ON THE FLOCCULATION OF FRESH HIDE  
PADDLE-VAT UNHAIRING WASTE

|                  | Removed by 2 hr Settling    |                             |                             |                              |
|------------------|-----------------------------|-----------------------------|-----------------------------|------------------------------|
|                  | Control <sup>a</sup><br>(%) | 0% NaCl <sup>b</sup><br>(%) | 2% NaCl <sup>b</sup><br>(%) | 5 % NaCl <sup>b</sup><br>(%) |
| Suspended Solids | 25.4                        | 86.5                        | 82.2                        | 79.4                         |
| Volatile SS      | 23.7                        | 85.3                        | 72.3                        | 78.9                         |

<sup>a</sup> No flocculant added.

<sup>b</sup> PFA-10, 3 mg/l of effluent.

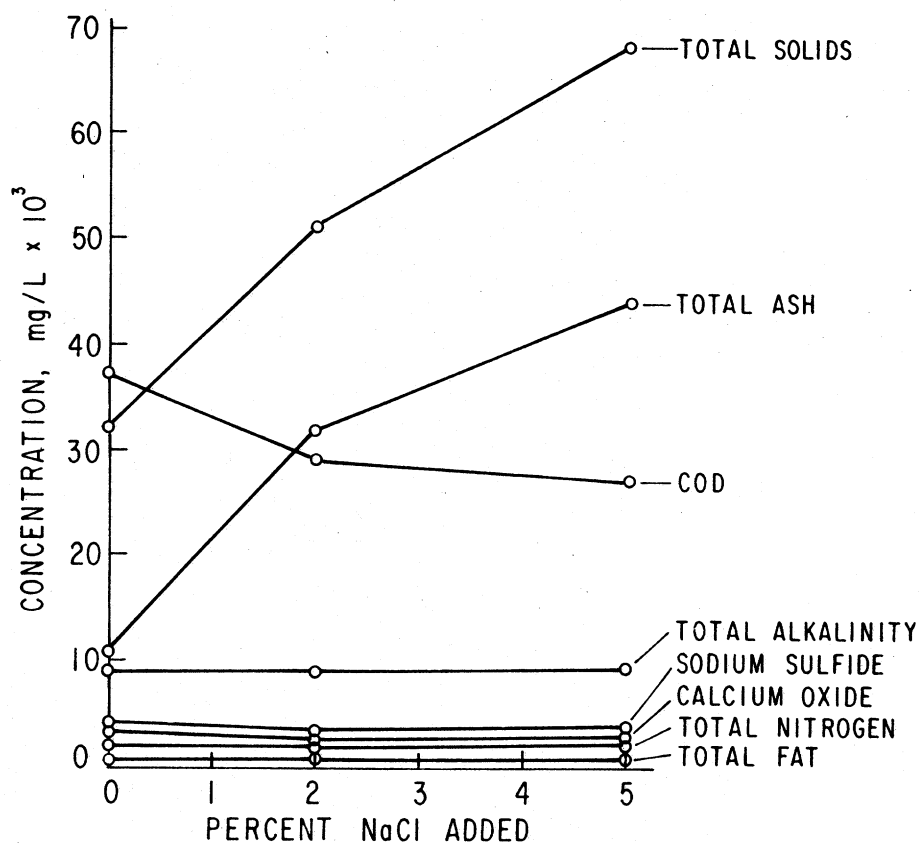


FIGURE 2.—Composition of supernatant liquor from flocculation of paddle-vat unhairing waste containing added salt.

period were detrimental to the flocculation of suspended solids, since the removal of suspended solids decreased from 90 percent initially to 66 percent at the 5 percent NaCl level and three weeks storage.

Table III summarizes the results of flocculating the suspended solids from fresh hides unhaired in a paddle vat. The data show the percentage reductions in the principal constituents and the composition of the settled solids. It is of interest to note that the principal constituent of the total ash is calcium oxide. The relatively high nitrogen and calcium oxide contents of the settled solids represent a potentially valuable source for fertilizer and/or feed mixes.

**TABLE III**  
**FLOCCULATION OF PADDLE-VAT UNHAIRING WASTE FROM FRESH HIDES**

|                  | Effluent<br>composition<br>(mg/l) | Removed by<br>2 hr settling |                                 | Composition<br>of settled<br>solids<br>(%)<br>MFB |
|------------------|-----------------------------------|-----------------------------|---------------------------------|---|
|                  |                                   | Control <sup>a</sup><br>(%) | Flocculated <sup>b</sup><br>(%) |   |
| COD              | 40,000                            |                             | 4.8                             |   |
| Total solids     | 46,000                            |                             |                                 |   |
| Suspended solids | 15,780                            | 25.4                        | 86.5                            |   |
| Volatile SS      | 10,770                            | 23.7                        | 85.3                            |   |
| Total alkalinity | 11,220                            |                             | 21.7                            |   |
| Sodium sulfide   | 4,530                             |                             | 9.0                             |   |
| Total nitrogen   | 3,710                             |                             | 21.2                            | 3.29  |
| Total fat        | 1,580                             |                             | 20.3                            | 4.14  |
| Total ash        | 17,550                            |                             | 38.0                            | 45.40   |
| Calcium oxide    | 5,890                             |                             | 70.2                            | 45.20   |
| Sodium chloride  | 1,000                             |                             |                                 |   |

<sup>a</sup> No flocculant added.

<sup>b</sup> PFA-10, 3 mg/l of effluent.

The effects of added salt on the flocculation of fresh hide paddle-vat unhairing waste are summarized in Table IV. Gravity settling reduced the suspended solids about 25 percent, and the PFA-10 reduced the suspended solids by 86 percent. The addition of 2 percent and 5 percent NaCl had very little effect on the flocculation of suspended solids and the volatile suspended solids.

The compositions of the supernatant liquors resulting from the flocculation of fresh hide paddle-vat waste to which salt was added is shown in Figure 2. The total solids and total ash contents increased as the amounts of added salt were increased, and the COD decreased. The concentrations of the other constituents were relatively unchanged.

Table V summarizes the results of flocculating the suspended solids from unhairing brine-cured hides in a paddle vat. The NaCl concentration of this waste was about 3 percent. About 14 percent of the suspended solids settled out in 2 hr, and 73 percent settled out as a result of the addition of PFA-10. The concentrations of total solids and total ash were higher than they were in the previous unhairing wastes, but the other constituents were present in concentrations comparable to those in the waste containing 5 percent added salt.

TABLE V  
FLOCCULATION OF PADDLE-VAT UNHAIRING WASTE FROM BRINE-CURED HIDES

|                  | Effluent<br>composition<br>(mg/l) | Removed by<br>2 hr settling |                                 | Composition<br>of settled<br>solids<br>(%)<br>MFB |
|------------------|-----------------------------------|-----------------------------|---------------------------------|---|
|                  |                                   | Control <sup>a</sup><br>(%) | Flocculated <sup>b</sup><br>(%) |   |
| COD              | 31,000                            |                             | 3.0                             |   |
| Total solids     | 107,000                           |                             |                                 |   |
| Suspended solids | 12,780                            | 13.9                        | 73.4                            |   |
| Volatile SS      | 6,380                             | 12.9                        | 63.3                            |   |
| Total alkalinity | 11,470                            |                             | 11.0                            |   |
| Sodium sulfide   | 4,580                             |                             | 15.1                            |   |
| Total nitrogen   | 2,650                             |                             | 20.2                            | 1.62  |
| Total fat        | 1,000                             |                             | 26.5                            | 0.70  |
| Total ash        | 87,000                            |                             | 34.9                            | 85.70   |
| Calcium oxide    | 2,260                             |                             | 22.0                            | 24.70   |
| Sodium chloride  | 32,700                            |                             |                                 |   |

<sup>a</sup> No flocculant added.

<sup>b</sup> PFA-10, 3 mg/l. of effluent.

Table VI summarizes the results of flocculating suspended solids from recycled unhairing waste resulting from unhairing brined hides in a drum. The NaCl concentration of this waste was about 7 percent. The concentrations of most of the constituents, such as total solids, nitrogen, ash, and CaO, are higher than they were in the previous unhairing wastes because they had been built up by the several recyclings this waste had been subjected to. It has been shown that lime-sulfide unhairing liquors can be recycled more than 20 times (11, 12), perhaps indefinitely. The only treatments necessary before reuse are replenishment with lime, sulfide, and water, preferably as washings from the previous unhairing operation. In this waste about 26 percent of the suspended solids settled out in 2 hr and 81 percent settled out as a result of the addition of PFA-10.

**TABLE VI**  
**FLOCCULATION OF RECYCLED DRUM UNHAIRING WASTE**  
**FROM BRINE-CURED HIDES**

|                  | Effluent<br>composition<br>(mg/l) | Removed by<br>2 hr settling |                                 | Composition<br>of settled<br>solids<br>(%)<br>MFB |
|------------------|-----------------------------------|-----------------------------|---------------------------------|---|
|                  |                                   | Control <sup>a</sup><br>(%) | Flocculated <sup>b</sup><br>(%) |   |
| COD              | 62,000                            |                             | 4.8                             |   |
| Total solids     | 129,000                           |                             |                                 |   |
| Suspended solids | 22,350                            | 25.8                        | 81.3                            |   |
| Volatile SS      | 13,870                            | 22.7                        | 81.6                            |   |
| Total alkalinity | 18,250                            |                             | 10.9                            |   |
| Sodium sulfide   | 4,320                             |                             | 13.5                            |   |
| Total nitrogen   | 9,630                             |                             | 13.7                            | 2.97  |
| Total fat        | 1,170                             |                             | 17.9                            | 2.55  |
| Total ash        | 62,300                            |                             | 18.7                            | 55.00   |
| Calcium oxide    | 4,890                             |                             | 10.0                            | 42.80   |
| Sodium chloride  | 69,100                            |                             |                                 |   |

<sup>a</sup> No flocculant added.

<sup>b</sup> PFA-10, 3 mg/l of effluent.

Table VII summarizes the results of flocculating wastes from the unhairing of cured hides in a hide processor. This tanner soaks and unhairs the hides in the same liquor, and the waste contains the salt from the soaking as well as the unhairing chemicals. The polyelectrolyte X-400 was used to promote flocculation in this waste. The compositions of the waste and the flocculated fractions are much higher than those of paddle-vat unhairing waste. Only the compositions of recycled drum unhairing waste (Table VI) approach the compositions of the hide processor waste. The NaCl concentration of this waste was about 8 percent. About 37 percent of the suspended solids settled out in 2 hr and about 95 percent was removed by the addition of X-400. The experimental results also show that the NaCl contents of the unhairing wastes did not inhibit the flocculating abilities of the polyelectrolyte used to remove the suspended solids.

Our previous work (3) showed that PFA-10 is not effective for flocculating the suspended solids in hide processor unhairing waste, nor is X-400 effective for flocculating the suspended solids in paddle-vat unhairing waste. The principal differences between the two wastes are the higher solids content and higher salt content of hide processor unhairing waste. We can only speculate, however, as to the reasons why a chemical flocculant is effective in one unhairing waste and not

TABLE VII

FLOCCULATION OF HIDE PROCESSOR UNHAIRING WASTE FROM SALT-CURED HIDES

|                  | Effluent<br>composition<br>(mg/l) | Removed by<br>2 hr settling |                                 | Composition<br>of settled<br>solids<br>(%)<br>MFB |
|------------------|-----------------------------------|-----------------------------|---------------------------------|---|
|                  |                                   | Control <sup>a</sup><br>(%) | Flocculated <sup>b</sup><br>(%) |   |
| COD              | 59,000                            |                             | 23.7                            |   |
| Total solids     | 208,000                           |                             |                                 |   |
| Suspended solids | 54,420                            | 37.5                        | 94.8                            |   |
| Volatile SS      | 23,000                            | 36.7                        | 90.8                            |   |
| Total alkalinity | 30,000                            |                             | 25.4                            |   |
| Sodium sulfide   | 8,610                             |                             | 33.5                            |   |
| Total nitrogen   | 6,430                             |                             | 9.0                             | 2.00  |
| Total fat        | 1,030                             |                             | 19.9                            | 1.89  |
| Total ash        | 152,300                           |                             | 31.4                            | 63.40   |
| Calcium oxide    | 20,070                            |                             | 59.0                            | 23.90   |
| Sodium chloride  | 81,300                            |                             |                                 |   |

<sup>a</sup> No flocculant added.<sup>b</sup> X-400, 5 mg/l of effluent.

in another. The selection of a particular chemical flocculant must be determined by trial on the unhairing waste.

The flocculated solids represent a potential source of material for fertilizer and/or feed mixes after processing by suitable drying and handling procedures. The supernatant liquor contains considerable quantities of dissolved constituents such as sulfides, inorganic salts, nitrogen compounds, and hair, fat, and albuminous matter. This liquor may be handled by various methods, *e.g.*, biological treatment or recycling for repeated unhairing, and thus conserve some materials and save on costs. The removal of COD, BOD, sulfides, and insoluble nitrogen compounds by further treatments will reduce environmental pollution and provide direct and indirect benefits to society.

### Summary and Conclusions

This work has shown that effective flocculating systems can be developed to remove suspended solids from unhairing waste. PFA-10 reduced the suspended solids of fresh hide paddle-vat unhairing waste about 80 to 85 percent. The addition of up to 5 percent NaCl caused only a moderate reduction in the removal of suspended solids. X-400 reduced the suspended solids of hide processor unhairing waste about 90 percent. Unhairing wastes from different unhairing

processes were successfully treated with chemical flocculants to remove suspended solids. The scale-up from laboratory to pilot plant has been demonstrated successfully and points the way to full-scale commercial application by tanneries.

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